



Characterization of nano-lead-doped active carbon and its application in lead-acid battery



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HIGHLIGHTS

- We researched the bad influences of AC used in lead-acid battery.
- Nano-Pb/AC inhibited HER through increasing the adsorption impedance of hydrogen.
- Nano-Pb/AC could overcome the negative effects of AC in lead-acid battery.
- Nano-Pb/AC in negative plate can improve the performances of lead-acid battery.

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ABSTRACT

In this paper, nano-lead-doped active carbon (nano-Pb/AC) composite with low hydrogen evolution current for lead-acid battery was prepared by ultrasonic-absorption and chemical-precipitate method. The nano-Pb/AC composite was characterized by SEM, EDS and TEM. The electrochemical characterizations are performed by linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) in a three-electrode system. Since intermediate adsorption is the rate-determining step, the hydrogen evolution reaction (HER) is markedly inhibited as the intermediate adsorption impedance of nano-Pb/AC increased. Meanwhile, the working potential of nano-Pb/AC is widened to the whole potential region of Pb negative plate (from -1.36 V to -0.86 V vs. Hg/HgSO_4) in lead-acid battery. In addition, nano-Pb can improve the interfacial compatibility between AC and Pb paste, accordingly relieve the symptoms of carbon floatation. Finally, 2.0 V single-cell flooded lead-acid batteries with 1.0 wt.% nano-Pb/AC or 1.0 wt.% AC addition in negative active materials are assembled. The cell performances test results show that the 3 h rate capacity, quick charging performance, high current discharging performance and cycling performance of nano-Pb/AC modified battery are all improved compared with regular lead-acid battery and AC modified lead-acid battery.

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1. Introduction

Batteries working under hybrid electric vehicle (HEV) service are exposed to a duty cycle, which is quite different from any other function that lead-acid batteries have been required to perform. The batteries operate at partial-state-of-charge (PSoC) rather than a fully charged condition, and charges and discharges tend to be of short duration but high rate. Under this condition, lead-acid batteries that have been designed for conventional tasks (e.g., SLI or deep cycle), fail rather quickly due to irreversible sulfation of negative plates [1].

For solving the above-mentioned problems, two different strategies were proposed. The one named lead–carbon battery (Pb–C

battery), which usually added some carbon materials into the negative paste. The other, combined an asymmetric supercapacitor and a lead-acid battery in a single unit, named UltraBattery. Nakamura [2] investigated the influence of small additions of certain (not specified) sorts of carbon into the negative paste for the first time and found a favourable effect on the hindrance of sulfation. The beneficial effect of carbon was attributed to the formation of conducting bridges through carbon particles surrounding the sulfate crystals. This idea was further elaborated by A.F. Hollenkamp and sponsored by ALABC [3]. It was found that the addition of up to 2% of carbon black or graphite powder into the negative paste could hinder the sulfation of negative electrodes. They observed that the addition of graphite to the negative active materials (NAMs) in the unformed state improved the conductivity of the plate. However, M. Calábek [4] opined that the improvement of the cycle life of negative plate was attributed to the inhibition of the

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growth of lead sulfate crystals deposited in the electrode pores, but not the improving of conductivity. Afterwards, D. Pavlov [5] discovered that the addition of electrochemical active carbon could decrease the overpotential of reaction $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$, which will improve the charge acceptance and discharging capacity of the negative electrode. Common-wealth Scientific and Industrial Research Organization (CSIRO) and Furukawa Battery developed the UltraBattery [6–8], which was reported to have the advantage of being long lasting, cost effective and more powerful than past technologies used in HEVs. The supercapacitor, acting as a buffer during high-rate discharge and charge, enhances the power and lifespan of lead-acid battery. Thus, the UltraBattery in HEVs is able to deliver and absorb charge rapidly during vehicle acceleration and regenerative braking, respectively. This technology has been described in literature in detail [8–10].

However, we must pay more attention to the harmful influences of carbon materials on lead-acid batteries. First, under the negative plate working conditions of lead-acid battery (−0.86 to −1.36 V vs. Hg/HgSO₄, 5 mol L^{−1} sulfuric acid), carbon materials will perform low capacity and serious hydrogen evolution [11] whether as negative additive or a single asymmetric supercapacitor. As a result, more gas will be given off towards the end of charging and cause the thermal runaway or even electrolyte dry-out [12,13]. Second, the addition of carbon will reduce the charge retention ability as a galvanic cell may form by Pb and C which have been testified in this paper. Moreover, bad miscibility, great differences in specific surface and gravity between C and Pb make them difficult to mix evenly. This may cause the carbon floatation and carbon penetration phenomenon, which would limit the beneficial effects of C. But up to now, few researches have been reported on these aspects.

In this paper, we prepared a nano-Pb/AC composite with low hydrogen evolution and good miscibility. Furthermore, hydrogen inhibition mechanism was evaluated by EIS. The electrochemical behavior of AC and nano-Pb/AC negative electrodes working in lead-acid battery was studied. Then, some single-cell flooded lead-acid batteries with AC or nano-Pb/AC additions were assembled. The performances including initial capacity, quick charging ability, high current discharging ability, hydrogen evolution rate and cycle life were tested in the ensuing experiments.

2. Experimental

2.1. Preparation of nano-Pb/AC composite

Nano-Pb/AC composite was prepared by the ultrasonic-absorption and chemical-precipitation method with three steps.

Pretreatment: 2g AC raw material (YP-50, produced by Japan Kuraray) was immersed in 100 mL 80% ethyl alcohol for 2 min.

Ultrasonic-absorption: 300 mL 0.1 mol L^{−1} Pb(NO₃)₂ solution was poured into the wetted raw material under ultrasonic oscillation for 10 min. Then the sample was filtered out and washed with deionized water.

Chemical-precipitation: The sample was dipped into 300 mL 0.1 mol L^{−1} H₂SO₄ solution under ultrasonic oscillation for 10 min, and then PbSO₄ was generated and precipitated in the pores. Followed by filtering and washing with deionized water to pH = 7.0, drying at 60 °C for 10 h, the nano-Pb/AC composite was obtained.

2.2. Preparation of testing samples

For electrochemical testing, AC paste (contents: 80 wt.% AC, 10 wt.% PVDF, 10 wt.% acetylene black) was evenly painted on Ti foil and then dried at 60 °C for 8 h. The working area was 1.0 cm × 1.0 cm.

For battery testing, a serial of 2.0 V single-cell flooded lead-acid batteries with one negative plate sandwiched between two PbO₂ positive plates were assembled. There were three kinds of negative plates, the common Pb paste negative plate for regular lead-acid battery (LB), the 1.0 wt.% (relative to the Pb active materials) blank AC addition in negative plate for AC modified lead-acid battery (ACLB) and the 1.0 wt.% nano-Pb/AC composite addition in negative plate for nano-Pb/AC modified lead-acid battery (nano-Pb/ACLB). All positive and negative plates had a size of 4.0 cm × 6.8 cm (height × width) and geometric area of 27.2 cm². The thickness was 0.30 cm for the positive plates and 0.20 cm for the negative plates. The positive plates and common negative plates were all produced by Henan Yuguang Gold & Lead Co., Ltd.

2.3. Instruments

The electrochemical experiments were carried out in a three-electrode system. The counter electrode was Pt plate with a geometric area of 16.00 cm². The mercury/mercurous sulphate reference electrode (Hg/HgSO₄) was used as the reference electrode. All potentials in this paper were reported with respect to this reference electrode unless specified. The electrolyte was 5 mol L^{−1} sulfuric acid solution.

Electrochemical experiments such as cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were performed using a PARSTAT 2273 electrochemical workstation controlled by the Powersuit software. The frequency interval of EIS measurement was from 10⁵ to 10^{−2} Hz, and the AC amplitude was 10 mV. Battery testing was performed using LAND battery test system. JEM-2010 Transmission Electron Microscope (TEM), JSM-6360F Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS) was used to observe the microscopic surface morphology and determine elementary composition of as-prepared nano-Pb/AC composite. Porous structure of the sample was tested by nitrogen adsorption/desorption isotherms at −196 °C with the Monosorb produced by Quantachrome Instruments Company. Content of Pb in nano-Pb/AC was analyzed with Inductively Coupled Plasma Atomic Emission Spectrometry (IRIS1000ICP) produced by Thermo Fisher Scientific.

3. Results and discussion

3.1. Properties of nano-Pb/AC composites

3.1.1. Characterization

Fig. 1 provides the morphology of AC and nano-Pb/AC characterized by SEM, EDS and TEM. It can be seen that both samples mainly consist of large AC lumps (2–10 μm) and plentiful small AC particles (less than 2 μm). This proves that no serious structural damage of AC occurred in this modification process. But, a small amount of tiny white particles can be observed in nano-Pb/AC composite (Fig. 1b). EDS testified that the white particles were Pb containing materials (Fig. 1d). As shown in Fig. 1c, the nano-Pb compound particles are found abundantly in AC particles with the size of 5–10 nm. The average content of Pb is about 3.32 wt.% measured by ICP.

The nitrogen adsorption/desorption isotherms of AC and nano-Pb/AC are shown in Fig. 2a. The isotherms are supposed to be type IV, which occurs on adsorbents possessing a mixture of microporosity and mesoporosity. The slope at the end of the isotherm was due to a limited uptake of nitrogen at higher relative pressures, indicating capillary condensation took place in mesopores [14]. The BET surface area of AC is 1528 m² g^{−1} and that of nano-Pb/AC is 1192 m² g^{−1}. Pore-size distributions gauged by HK mode (for micropores) and BJH mode (for mesopores) are shown in

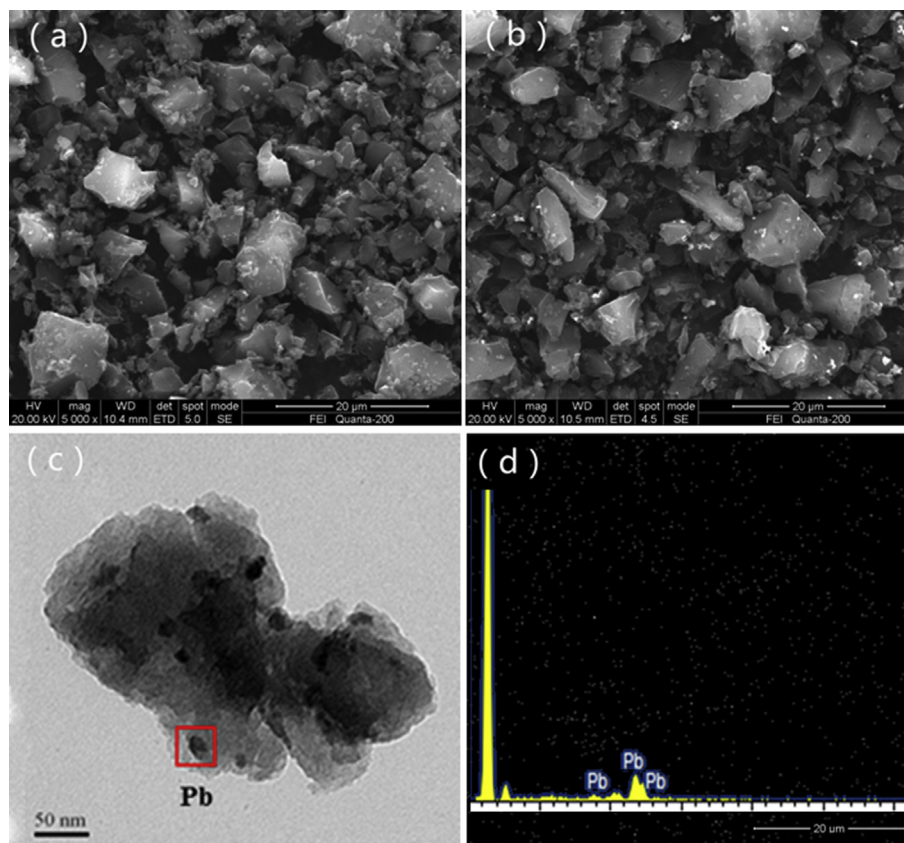


Fig. 1. Morphology of AC and nano-Pb/AC composites (a. SEM image of AC, b. SEM image of nano-Pb/AC, c. TEM image of nano-Pb/AC composites, d. Pb area scanning of nano-Pb/AC by EDS).

Fig. 2b and c, respectively. According to the test results, it was found that nano-Pb modification decrease AC's pore volume in the whole range. This indicates that nano-Pb compound may absorb on the surface of the pores (whatever micropore or mesopores) and blocked/narrowed these pores, which can be well adduced to explain the fall in the BET surface area of nano-Pb/AC.

3.1.2. Capacity

Fig. 3 presents the cyclic voltammetry (CV) curves between -1.36 V and -0.86 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) at 25°C in $5\text{ M H}_2\text{SO}_4$ solution, the scanning rate was fixed at 10 mV s^{-1} . Generally, each redox peak corresponds to an electrochemical reaction on CV curves. Pb often oxidizes to PbSO_4 under -0.9 V, but there is no observed Pb redox peak on the CV curves of nano-Pb/AC electrode, as the Pb content in nano-Pb/AC composite is very low and the reaction current of Pb/Pb^{2+} is too small to be detected. Thus, only hydrogen evolution reaction and double layer charging/discharging process were observed on the CV curves.

We all know that the supercapacitor mainly acts as a current buffer in UltraBattery during high-rate discharge and charge to enhance the power and lifespan of battery. The original AC must not be a good buffer to share the charge/discharge current effectively, because the charge separation/neutralization of AC can only occurs above -1.16 V. This means that during early stages of discharge, the current mainly comes from the Pb negative plate and only little from the capacitor electrode owing to its higher charge-neutralization potential, this problem also reported in detail by L.T. Lam [9]. Obviously, the charge separation/neutralization potential of nano-Pb/AC is widened to the whole potential range of negative plate, this means nano-Pb/AC can conquer this shortcoming and act as a better buffer.

In addition, the capacity also determined the buffer performance of the supercapacitor working in UltraBattery. The specific capacity of AC material was often calculated by the following formulas:

$$C_m = \frac{1}{mv\Delta V} \int_{V_1}^{V_2} I(V)dV$$

where, C_m is the specific capacitance (F g^{-1}), m is the mass of active material in the working electrode (g), v represents the scanning speed (V s^{-1}), ΔV is the width of the potential window (V), and $\int_{V_1}^{V_2} I(V)dV$ is the integral area of CV curves. As shown in Fig. 3, nano-Pb/AC composite exhibits a capacity performance of 43.38 F g^{-1} , which is 43.1% higher than that of AC (30.31 F g^{-1}).

3.1.3. Hydrogen evolution performance

LSV curves of AC, nano-Pb/AC composite and pure Pb electrodes with the same apparent working area are presented in Fig. 4. When the potential is lower than the onset potential of hydrogen evolution, hydrogen evolution current exponentially increases with the potential negatively shifted. The onset potential of hydrogen evolution is -1.14 V for nano-Pb/AC electrode, but -1.02 V for AC, -1.23 V for pure Pb. However, the hydrogen evolution current of nano-Pb/AC electrode is -8.07 mA cm^{-2} under -1.36 V, which is only 16% of AC (-50.59 mA cm^{-2}), and just 118% of the pure Pb (6.83 mA cm^{-2}). It states that the modification of nano-Pb has great restraint action on hydrogen evolution and the hydrogen evolution performance is even close to the pure Pb electrode.

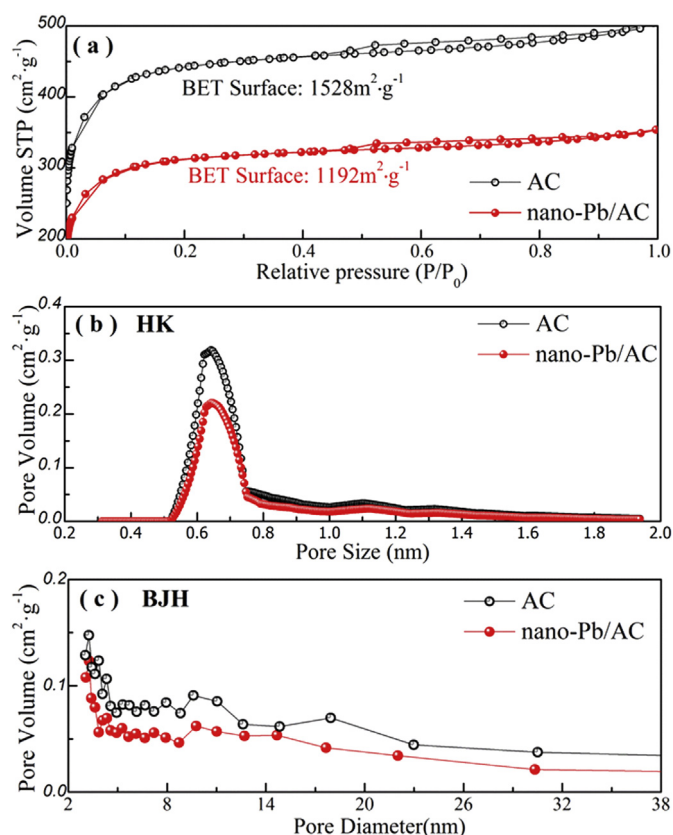


Fig. 2. Nitrogen adsorption/desorption isotherms (a) and pore-size distributions (b, c) of AC and nano-Pb/AC.

Electrochemical impedance spectroscopy is a powerful method that is very often used to elucidate the HER mechanism. It is well known that HER proceeds through three steps [15]: electrochemical adsorption – the Volmer reaction, and two possible desorption steps: electrochemical desorption – the Heyrovsky reaction and chemical desorption – the Tafel reaction. The equivalent electrical circuit (EEC) proposed by Armstrong and Henderson [16] for modeling the impedance of HER is shown in Fig. 5a. Where, R_e is the sum of electrode resistance and solution resistance; C_{dl} is the

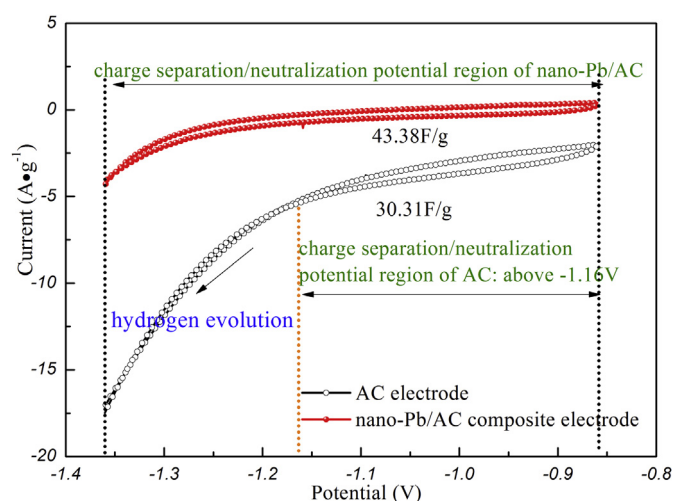


Fig. 3. CV curves of AC and nano-Pb/AC electrodes (sweep rate: 10 mV s⁻¹, electrolyte: 5 M H₂SO₄, temperature: 25 °C).

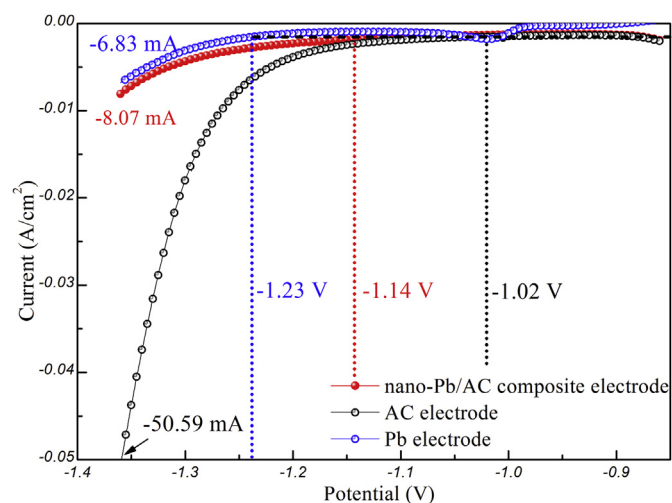


Fig. 4. LSV curves of various electrode (sweep rate: 1.0 mV s⁻¹, electrolyte: 5 M H₂SO₄, temperature: 25 °C).

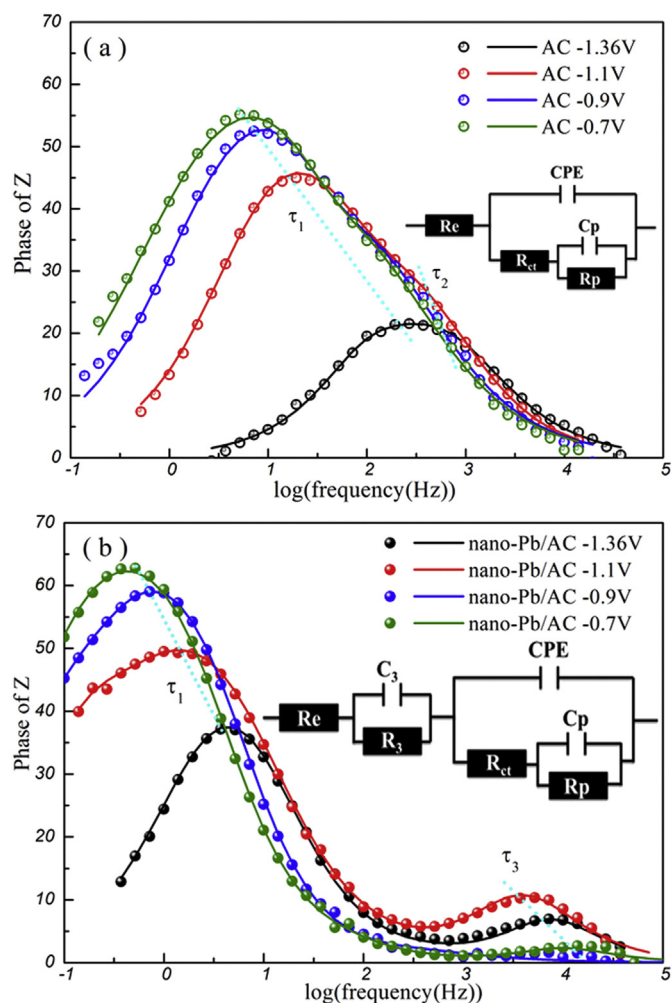


Fig. 5. The Bode diagram and equivalent electrical circuits of (a) blank AC and (b) nano-Pb/AC electrodes under -0.7 V, -0.9 V, -1.1 V, -1.36 V, (electrolyte: 5 M H₂SO₄, temperature: 25 °C).

double-layer capacitance, R_{ct} denotes the charge transfer resistance of electrochemical desorption step; C_p is the adsorption capacitance, R_p is the adsorption resistance of hydrogen. The double-layer capacitance was replaced by a constant phase element (CPE) for AC electrode, which has a porous structure. And $Z_{CPE} = (1/Q)(j\omega)^{-n}$, here, $j = (-1)^{1/2}$ and n represents the deviation from the ideal behavior ($n = 1$ for the perfect capacitors and $n = 0$ for the pure resistors). The parameter Q is related to the average double-layer capacitance C_{dl} by the relation $C_{dl} = (Q/(R_{ct})^{n-1})^{1/n}$. From the double-layer capacitance C_{dl} , the real electrode surface area can be estimated [17,18].

The impedance parameters of nano-Pb/AC and AC electrodes were measured potentiostatically under -0.7 V, -0.9 V, -1.1 V and -1.36 V over a wide range of frequencies (10^{-1} Hz to 10^5 Hz) in 5 M H_2SO_4 solution. Fig. 5 shows the Bode diagram of nano-Pb/AC and blank AC electrodes at different potentials. Nyquist diagram usually consists of two partly overlapped capacitive semicircles for HER and accordingly two time constants appear in the Bode diagram [19–21]. The semicircle in the high frequency (HF) region can be related to the combination of charge transfer resistance and the double layer capacitance. The low frequency (LF) semicircle is related to the adsorption of intermediates on the electrode surface [22]. But the HF semicircle is difficult to identify in the Bode diagram of AC electrode because there is a strong overlap between the

two circles. The HF semicircle is also not found in nano-Pb/AC electrode (Fig. 5b), but unlike the AC electrode, this may because that the resistance value is too low to identify. However, a new time constant is obviously observed in nano-Pb/AC electrode. We guess this new semicircle in the higher frequency region (10^4 Hz) represents the reaction of Pb/Pb^{2+} for its resistance increased as the potential away from the equilibrium potential (about -1.0 V), while R_p and R_{ct} for HER are often continuous decreased as the potential negatively shifts [23]. So, a new (RC) loop represents the reaction of Pb/Pb^{2+} should be added into the EEC of nano-Pb/AC electrode (Fig. 5b), in which C_3 and R_3 is capacitance and charge transfer resistance of Pb/Pb^{2+} reaction, respectively.

Fig. 6 shows the Nyquist diagram of nano-Pb/AC composite and blank AC at different potentials. Parameter values obtained by fitting the EIS experimental data of the investigated electrodes at various potentials using the corresponding EECs are given in Table 1. It is found that R_{ct} and R_p both decreases while the potential negative shifts, which is coincide with the research of I. Herraiz [23]. For this reason, HER current of AC and nano-Pb/AC increases with the potential negative shifts in LSV curves. In HER process, R_p is much higher than R_{ct} at low potentials, which indicates that the rate-determining step of HER reaction is the electrochemical adsorption step. But for AC, it may shift to the electrochemical desorption step control when the potential is lower. The R_p value of

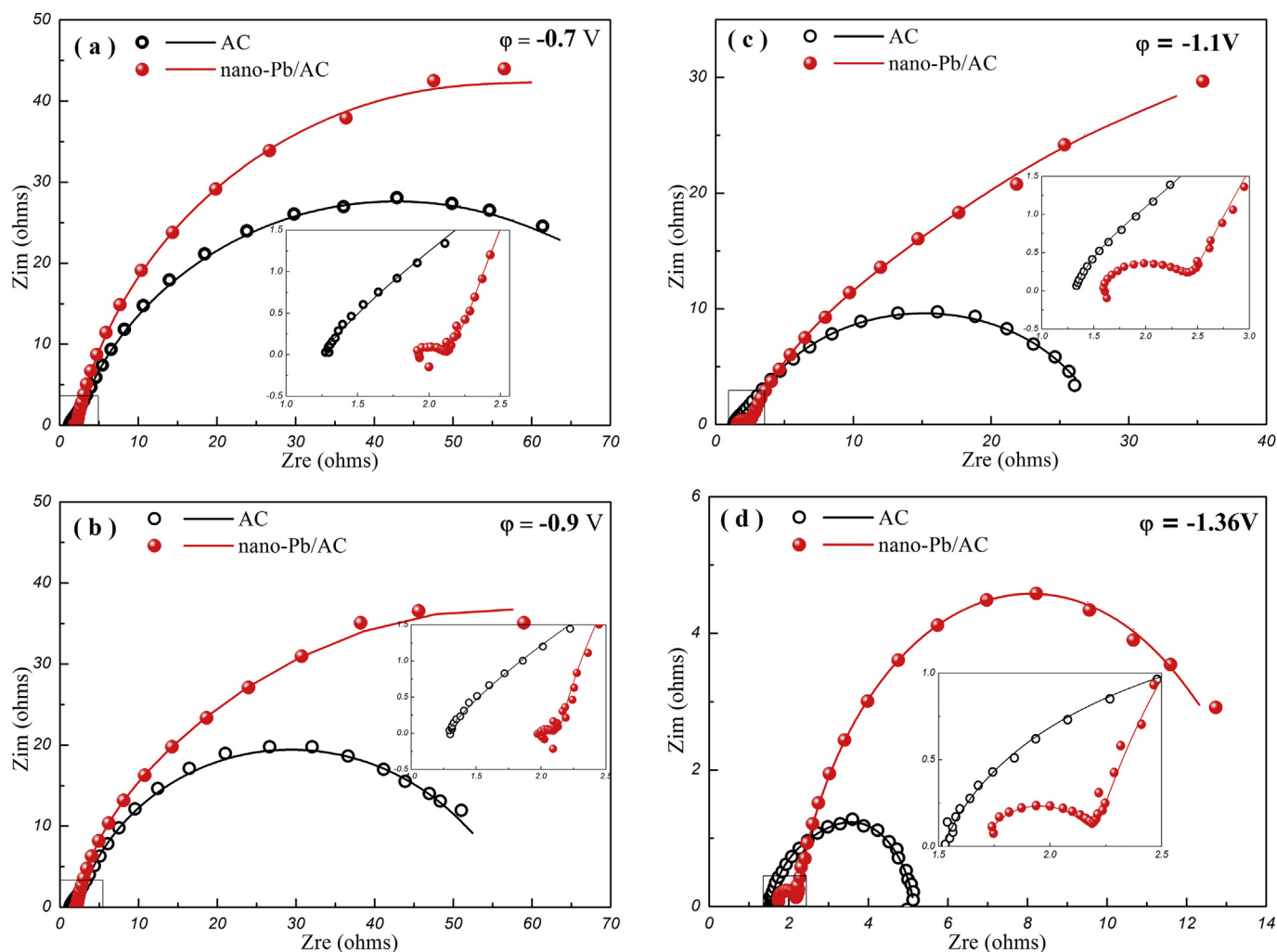


Fig. 6. The Nyquist diagram of blank AC and nano-Pb/AC electrodes under different potentials: (a) -0.7 V, (b) -0.9 V, (c) -1.1 V, (d) -1.36 V, electrolyte: 5 M H_2SO_4 , temperature: 25 °C.

Table 1

Fit parameters for AC and nano-Pb/AC electrode.

	η (V)	R_e (Ω)	Q (F)	n_1	C_{dl} (F cm ⁻²)	R_{ct} (Ω)	R_p (Ω)	C_p (F cm ⁻²)	R_3 (Ω)	C_3 (F cm ⁻²)	χ^2
AC	0.7	1.238	4.58E-2	0.80	0.0389	11.43	72.89	4.93E-4			6.01E-4
Nano-Pb/AC		1.948	2.57E-2	0.83	0.0130	1.407	105.7	3.70E-3	0.158	1.01E-4	4.53E-4
AC	0.9	1.263	3.67E-2	0.81	0.0288	9.757	47.19	5.70E-4			7.12E-4
Nano-Pb/AC		2.037	2.33E-2	0.82	0.0107	1.269	103.6	8.10E-3	0.484	1.10E-4	6.93E-4
AC	1.1	1.319	1.61E-2	0.81	0.0080	3.23	23.49	6.21E-4			2.03E-4
Nano-Pb/AC		1.606	1.87E-2	0.79	0.0061	0.79	52.3	2.73E-3	0.514	6.22E-5	7.02E-4
AC	1.36	1.52	9.9E-3	0.80	0.0040	2.639	1.997	1.28E-3			2.34E-4
Nano-Pb/AC		1.714	1.2E-2	0.82	0.0040	0.583	11.36	1.23E-3	0.646	5.23E-5	1.82E-4

nano-Pb/AC is much higher than AC at the same potential, which indicates that the AC modified by nano-Pb compounds could increase the adsorption resistance of hydrogen and inhibits the hydrogen evolution. In addition, the C_{dl} of nano-Pb/AC is obviously lower than AC. It means that Pb compounds clogged the pores and reduced the specific surface area of AC, which confirmed the BET test results. This also makes some contribution to the decreasing of the HER current.

3.1.4. Electrochemical behavior of AC in UltraBattery

A large number of researches concerning the influence of carbon adding in lead-acid battery have been carried out. But it was incapable of studying the electrochemical behavior of carbon directly due to the mixing C–Pb paste is impartible. Therefore, all the comments about electrochemical behavior of carbon in lead-acid battery were based on conjectures. Taking into account of the cell's structure, in part, Pb–C battery can be regarded as many little UltraBatteries grouped together. Herein, it was very convenient for us to study the electrochemical behavior of AC since Pb and AC electrode was separate in UltraBattery.

In this paper, ACUB (UltraBattery with one Pb negative plate, one AC capacitive negative plate, and a PbO₂ positive plate between them) and nano-Pb/ACUB (The same structure with ACUB while the capacitive negative plate was changed to nano-Pb/AC) were assembled. All negative plates had a size of 4.0 cm × 6.8 cm (height × width) and geometric area of 27.2 cm². The current distribution between the Pb negative plate and capacitor negative plate in a charge–discharge cycle were tested (as shown in Fig. 7), the regular lead-acid battery (LB) was used as the reference.

3.1.4.1. Charge step. It is noted that the AC negative plate takes much of the charge current in ACUB. By integral calculation, we find that the accepted capacity of Pb negative plate is only about 952.8 mAh while AC capacitor consumes about 1627.5 mAh in the whole charge process. The capacities of AC and nano-Pb/AC negative plates were tested by charge–discharge cycles at a constant current of 100 mA g⁻¹ in 5 M H₂SO₄ solution (as shown in Fig. 8). However, the capacity of AC negative plate is only 49 mAh, it indicates that most charging energy was wasted by hydrogen evolution. For this reason, the charging acceptance may decrease and the water loss will be exacerbated. This can also well explain the question why high content of AC decelerates the electrochemical processes of Pb formation [24]. However, the charge behavior of nano-Pb/ACUB is entirely different from ACUB but similar to LB. The total charging capacity is 1906 mAh, among which, nano-Pb/AC negative plate consumes only 170.7 mAh (the real capacity is about 105.6 mAh) and about 91% charging energy (1735.2 mAh) is accepted by Pb negative plate, which means little charging energy is wasted and the decrease of charging acceptance is effectively relieved.

3.1.4.2. Standing step. It's astonishing that AC negative plate is charged by Pb negative plate with an inner self-discharge current

about 25–40 mA in the whole standing loop in ACUB. Besides, we can obviously observe the gas evolution from AC negative plate. This attests a never reported phenomenon that a galvanic cell is formed between Pb and AC plates and the self-discharge rate of the cell may increase dramatically. The inner self-discharge current is also observed in nano-Pb/ACUB, but the value decreases to a neglectable level (0–1 mA).

3.1.4.3. Discharging step. L.T. Lam [9] noted that the capacitor would enhance the power and lifespan of the lead-acid battery as it acts as a buffer in discharging and charging. But this behavior may be restrained by the properties of AC. During early stages of discharge, the current mainly comes from the lead-acid negative

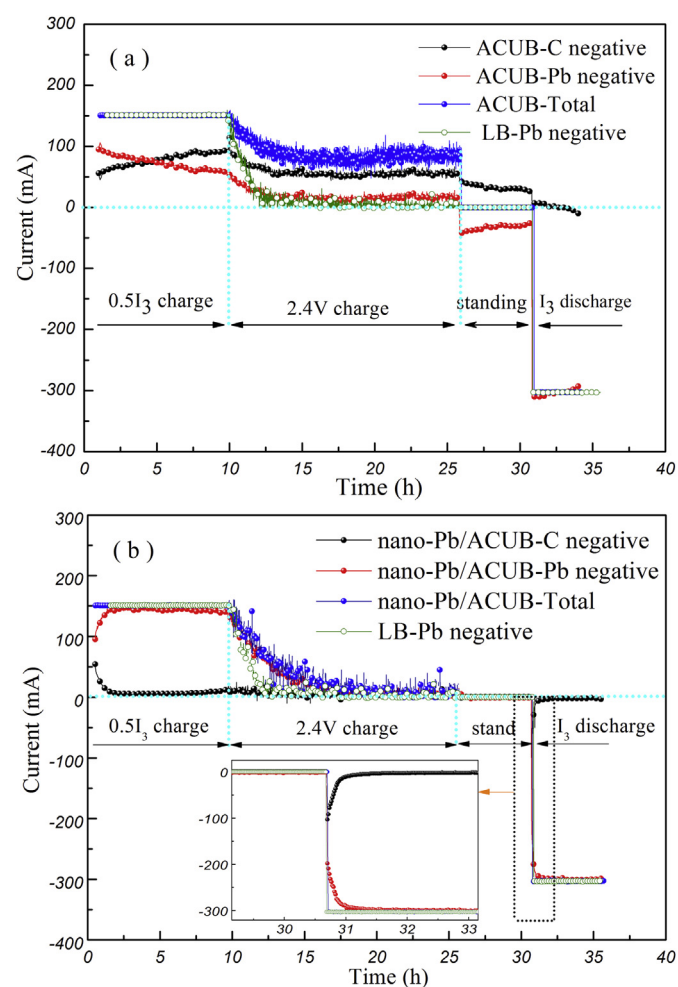


Fig. 7. Current distribution in Pb and C negative plates of (a) ACUB and (b) nano-Pb/ACUB (electrolyte: 5 M H₂SO₄, temperature: 25 °C).

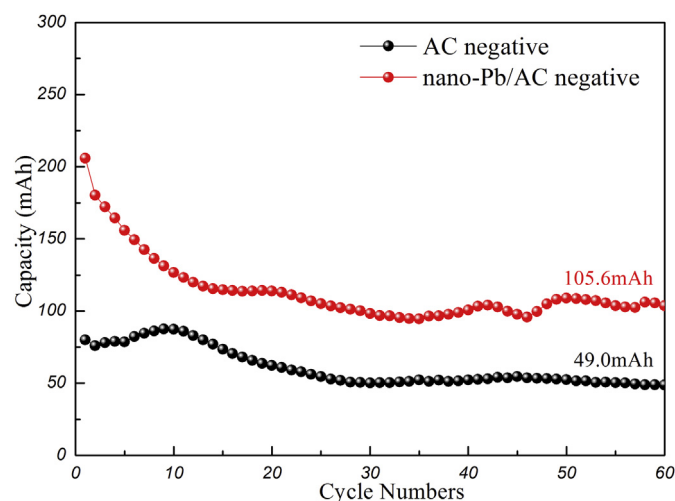


Fig. 8. Cycle capacities of AC and nano-Pb/AC negative plates.

plate and only little from the capacitor plate owing to its higher charge-neutralization potential. This inference is confirmed here, and it would be worse. In the ACUB, AC negative plate is even charged by Pb negative plate during the early state of discharge, and starts to discharge just when the ACLB is brought to 60% SoC. Obviously, this is not the desirable condition. Fortunately, this problem is overcome by nano-Pb/AC and a large discharge current from capacitor electrode is observed at the beginning of discharge process. It indicates that nano-Pb/AC could act as a good buffer in discharging and charging process, as its working potential window is better compatible with Pb negative plate. These conclusions are in good agreement with CV measurement results.

3.2. Application of nano-Pb/AC composites in lead-acid battery

Through the above discussion, we can confirm that ordinary commercial AC has a large hydrogen evolution current when working under a lead-acid battery's negative circumstance. It may have some strong negative effects on charge acceptance and charge retention ability of battery. However, as HER is markedly inhibited by nano-Pb/AC, to be sure, the positive effect of AC is worth to be looking forward. Thus, two kinds of negative-limit-capacity flooded lead-acid single cells which respectively used 1.0 wt.% nano-Pb/AC and common AC as the negative additives were produced and the performances including 3 h rate capacity, quick charging performance, high current discharging performance were investigated.

3.2.1. The morphology of Pb–C paste

High specific surface area of AC, different specific gravity and bad miscibility between AC and Pb make them difficult to mix evenly. For this reason, some carbon will divorce from the mixture and float on the solution when 5 M H_2SO_4 is injected, which is usually named carbon floatation phenomenon.

1.0 wt.% AC or nano-Pb/AC was added in Pb powder, after dry-mixing and mechanical stirring for 30 min, the AC-Pb and nano-Pb/AC-Pb pastes were obtained. The morphology of both pastes were evaluated by SEM (as shown in Fig. 9). It is observed that there are many isolated AC lumps within Pb powder in AC-Pb paste (Fig. 9a). However, the nano-Pb/AC lumps are almost completely covered by Pb powder (Fig. 9b). Furthermore, 1.0 g AC-Pb and nano-Pb/AC-Pb pastes were respectively weighted and dropped in 5 M H_2SO_4 for 24 h. The results were shown in the inserts of Fig. 9. For the specific gravity of AC was comparatively small, AC lumps

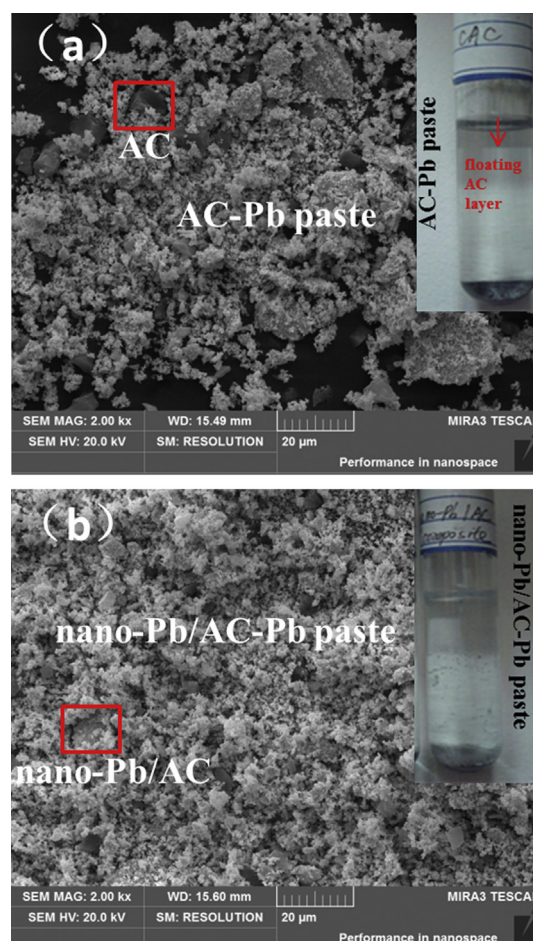


Fig. 9. Morphology of Pb pastes with (a) AC and (b) nano-Pb/AC.

without Pb sorbent quickly floated onto the surface and formed a floating AC layer (Fig. 9a). The floated AC may cause short circuit and result in permanent damage of the cell. But virtually no nano-Pb/AC lumps floated. This indicates that nano-Pb/AC has a better miscibility with Pb paste, and it can restrain the carbon floatation phenomenon and guard against the short circuit phenomenon.

The tapped densities of Pb, AC-Pb and nano-Pb/AC-Pb pastes were tested by FT-100B tap density tester after 2000 times vibration, which are 4.523 g cm^{-3} , 4.131 g cm^{-3} and 4.168 g cm^{-3} , respectively. The addition of AC and nano-Pb/AC decreases the tap density of the paste, which means that AC or nano-Pb/AC materials may act as light-weight skeletons in negative plate and increase the porosity of the Pb paste, and then promote the migration of ions. Besides, the tapped density of nano-Pb/AC-Pb paste is a little higher than that of AC-Pb paste, which proved that nano-Pb modification is conducive to mix AC with Pb paste evenly, this may better perform its functions in lead-acid battery.

3.2.2. The 3 h rate capacity test (C_3)

The profile of the 3 h rate capacity test consists of the following processes: (i) Fully charged at a constant current of $0.5I_3$ A to 2.4 V followed by a constant voltage of 2.4 V for 16 h (I_3 was gotten by calculation according to design capacity); (ii) Standing at open-circuit for 5 h; (iii) Discharging at a constant current of I_3 A to the cut-off voltage of 1.65 V.

Each cell was subjected to 10 subsequent capacity cycle tests at room temperature. The 10th discharge curve is shown in Fig. 10.

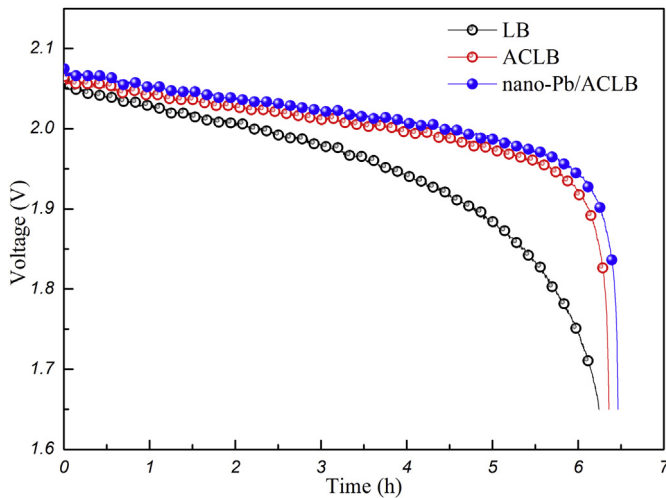


Fig. 10. Initial capacity test curves of lead-acid battery.

The 3 h rate capacities of the nano-Pb/ACLB, ACLB and LB are 1616.9 mAh, 1589.2 mAh and 1562 mAh, respectively. Then, we can obtain the mass specific capacity and the utilization of NAMs (as shown in Table 2). The specific capacity of nano-Pb/ACLB is 102.6 mAh g^{-1} , which is 2.5% higher than LB and 0.4% higher than ACLB. In addition, the utilization of NAMs is 41.92% for nano-Pb/ACLB, which is higher than LB (40.91%) and ACLB (41.78%).

The voltage of lead-acid battery is positively related to the sulfuric acid concentration at the reaction interface. Theoretically speaking, the battery voltage will slowly decrease while Pb^{2+} combines with SO_4^{2-} and the sulfuric acid consumes in the discharging process. But actually, the voltage often declines much faster because the sulfuric acid at the reaction interface cannot be replenished promptly by the bulk solution as the migration rate of SO_4^{2-} ions are relatively slow, just like the discharge curve of LB in Fig. 10. However, The obtained results evidenced that the discharge voltage curve of nano-Pb/ACLB was more stable and higher than LB, and so was ACLB. This phenomenon indicates that both AC additives with high BET surface area may improve the migration of ions, which may attribute to the lower tapped density and higher porosity of the paste as mentioned above.

3.2.3. High current discharging performance

High current discharging performance is an important battery feature in HEV concepts, as battery is aimed at assisting conventional engines during vehicle acceleration and to store energy from regenerative braking. The profile of the quick discharging ability test consists of following processes: (i) Fully charged at a constant current of 0.5I_3 A to 2.4 V followed by a constant voltage of 2.4 V for 16 h; (ii) Standing at open-circuit for 5 h; (iii) Discharging at a constant current of 4I_3 A to the cut-off voltage of 1.50 V.

In the high current discharging process, Pb dissolves to Pb^{2+} ions and reacts with SO_4^{2-} ions quickly, then the concentration of sulfuric acid decreases rapidly at the reaction interface due to the SO_4^{2-} ions couldn't be sufficiently supplied from the bulk solution.

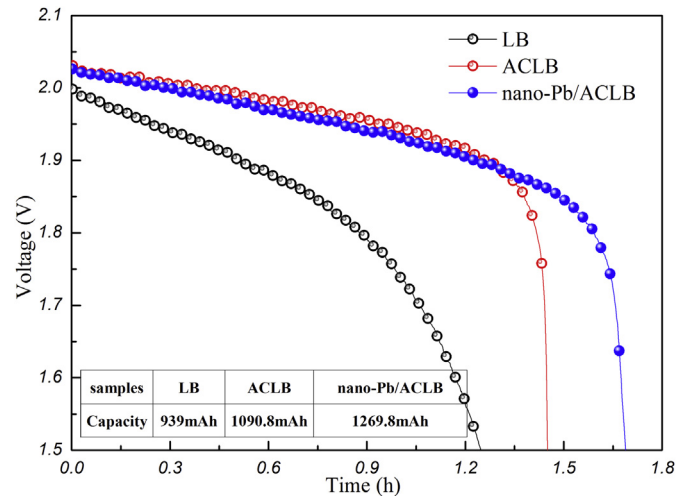


Fig. 11. Quick discharging ability tests of lead-acid batteries.

Correspondingly, the voltage decreases fleetly. At the same time, the high concentration Pb^{2+} ions would speed up the crystal growth of PbSO_4 on the surface of the plate, and the formed large PbSO_4 particles will block the ions migration channel and hinder the discharging of inner active materials. Thus, the capacity of lead-acid battery decreases in high rate discharging process. Fig. 11 shows the quick discharge curves for LB, ACLB and nano-Pb/ACLB at 4I_3 A. The quick discharge capacity of ACLB is 1090.8 mAh that is 16.2% higher than LB. This result is largely in line with previous researches. L.T. Lam [25] considered that carbon acted as an electro-osmotic pump that facilitated acid diffusion in the inner NAM volume at the high rates charge and discharge strategy. P.T. Moseley [26,27] noted that carbon with a high surface area might impede the growth of lead sulfate crystals. These all help to block the passivation of negative plate and improve the high current discharging capacity. Furthermore, nano-Pb/AC composite is likely to reinforce these favourable effects as the capacity is raised to 1269.8 mAh.

3.2.4. Quick charging performance

The profile of the quick charging performance test consists of the following processes: (i) Discharging at a constant current of I_3 A to the cut-off voltage of 1.65 V after fully charged; (ii) Charging at a constant current of 6I_3 A to 2.5 V followed by a constant voltage of 2.5 V, the time for the two charging steps was 1 h in total; (iii) Standing at open-circuit for 5 h; (iv) Discharging at a constant current of I_3 A to the cut-off voltage of 1.65 V.

As show in Fig. 12, the charge voltage of ACLB and nano-Pb/ACLB increase relatively slow and more energy is stored comparing with LB. It indicates that the quick charging performance is improved by both carbon additives. This result is in contradiction with the previous comment that AC may be harmful to the charge acceptance because of the serious hydrogen evolution. Does the excessive hydrogen evolution phenomenon no longer exist in Pb–C battery?

The negative plates were taken out from the batteries and polarized for a long time under -1.36 V in $5 \text{ M H}_2\text{SO}_4$. The

Table 2
Capacity of 2.0 V flooded lead-acid batteries (C_3).

	Negative plate (g)	Negative grid (g)	Negative active materials (g)	3 h rate capacity (mAh)	Utilization of active mass (%)	Negative mass specific capacity (mAh g^{-1})
LB	25.04	9.44	15.60	1562	40.91	100.1
ACLB	25.22	9.68	15.54	1589.2	41.78	102.2
Nano-Pb/ACLB	24.88	9.12	15.76	1616.9	41.92	102.6

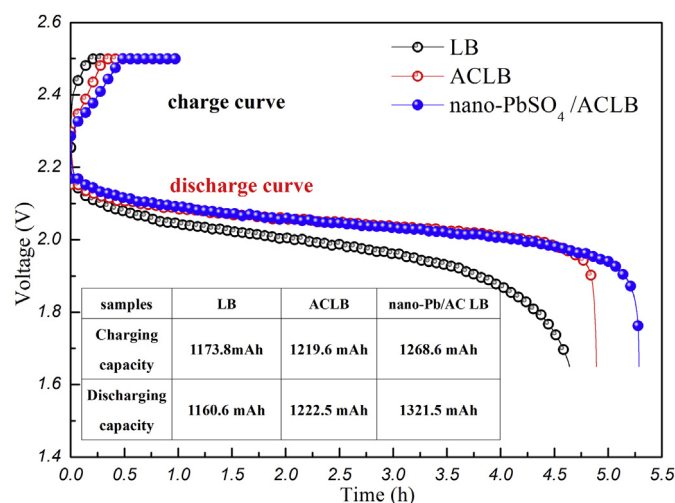


Fig. 12. Fast charging ability tests of lead-acid batteries.

polarization curves are shown in Fig. 13. It can be noted that there is a visible increasing of hydrogen evolution when 1.0 wt.% AC added. Thus, excessive hydrogen evolution also exists in Pb–C battery and makes the illusion that ACLB store more energy as nano-Pb/ACLB do, this is why the discharging capacity of nano-Pb/ACLB is higher than ACLB. In addition, it must be noted that AC is also an expander-like additive besides a capacitor [24,28], which can improve the migration of ions in the paste by increasing its porosity and may be beneficial to the charge acceptance. Moreover, this effect should be more obvious in flooded Pb–C battery, when the harmful influences of HER was restrained by the excess solution. Compared with ACLB, for one thing, the harmful influence was dispelled in nano-Pb/ACLB through inhibiting the HER (Fig. 12). For another, better compatibility may ameliorate the distribution of carbon and better perform its functions in lead-acid battery. Then, the best charge acceptance was obtained in the cell containing nano-Pb/AC.

3.2.5. Cycling performance

The evaluation of battery cycle-life is the time-consumed process. In the interests of expediency, the simplified discharge and charge profile which is often used to evaluate the endurance of battery in HEVs was adopted in this study. The profile composes of a

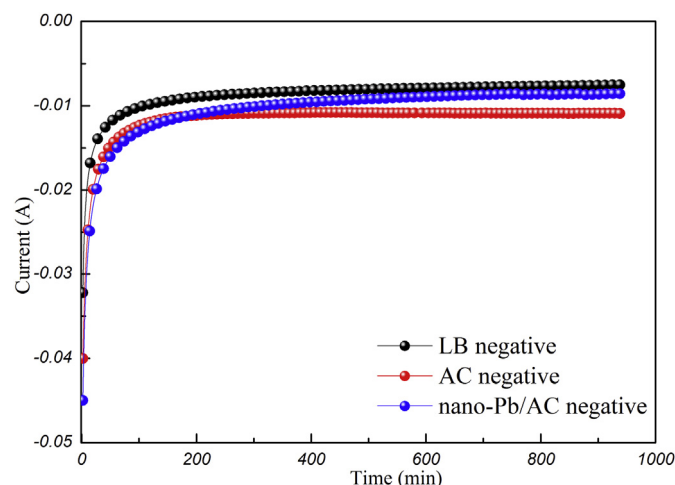


Fig. 13. Polarization curves of negative plates under -1.36 V in 5 M H_2SO_4 .

discharge at $2.5C_5$ A for 30 s and a charge at a constant voltage of 2.5 V with maximum current of $2.5C_5$ A for 31 s. Between each discharge and charge step, a rest time with 7 s was arranged. The fully charged cells were discharged at I_3 A rate to 50% SoC and then subjected repetitively to this profile at $25^\circ C$ until the voltage of each cell reached 1.77 V.

As shown in Fig. 14, the end-of-discharge voltage (EoDV) of the LB reached the cut-off voltage at 40,663 cycles. On the other hand, the ACLB using negative plate doped with commercial AC completed 70,739 cycles, which is about 1.7 times longer than that of the LB. As expected, the nano-Pb/ACLB achieved 95,863 cycles, which is much longer than LB and ACLB. This result indicates that the addition of nano-Pb/ACLB into NAMs can inhibit the irreversible sulfation of lead-acid battery and extend the lifespan of lead-acid battery greatly.

4. Conclusion

Under the working conditions of Pb negative plate in lead-acid battery, the ordinary commercial AC has a large hydrogen evolution current. For this reason, charging acceptance may decrease and the water loss will be exacerbated. A galvanic cell is formed between Pb and AC plates under standing loop, and then the self-discharge rate may increase dramatically. Furthermore, because the charge separation/neutralization potential of AC is higher than -1.16 V, AC capacitor is charged by Pb negative plate at the early discharging period, it may restrain the buffer effect of AC in UltraBattery.

Nano-Pb/AC composite for enhancing the performances of lead-acid battery was prepared in this paper. As the nano-Pb compound adsorbs on the surface of the AC pores, the adsorption impedance of hydrogen increases, the HER current of nano-Pb/AC composite decreases about 80% at -1.36 V compared with AC. The galvanic effect is almost eliminated and the inner self-discharge current decreased to $0-1$ mA as the hydrogen evolution being significantly restrained. In addition, the charge separation/neutralization potential of nano-Pb/AC composite is widened to the whole potential region of Pb negative plate, nano-Pb/AC capacitor could discharge at the early state of discharge with a high current and could act as a good buffer in battery.

For one thing, AC's negative effects are dispelled through inhibiting the HER. For another, nano-Pb/AC alters the structure of Pb paste and significantly improves the migration of ions. The

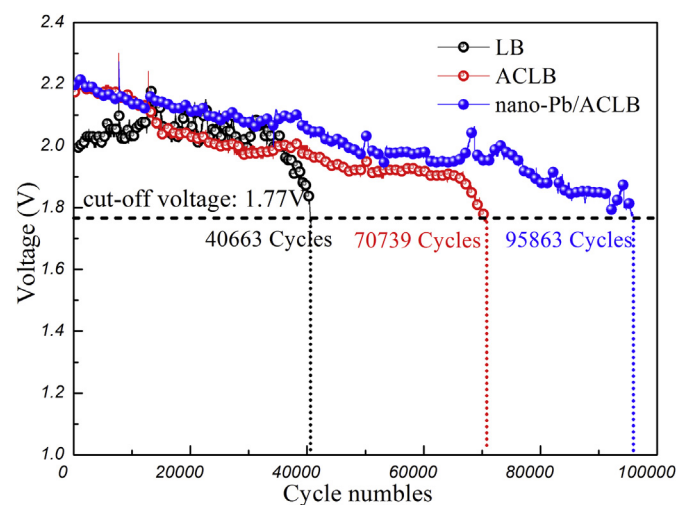


Fig. 14. Cycling performance of the ACLB and nano-Pb/ACLB under simplified discharge and charge profile.

performances of nano-Pb/ACLB including 3 h rate capacity, quick charging performance, high current discharging performance and cycling performance were all obviously improved compared with ACLB.

The present study suggests that nano-Pb/AC composite material prepared by ultrasonic-absorption and chemical-precipitate method is suitable for application in Pb–C battery or UltraBattery. During the practical production, to prevent the serious hydrogen evolution, the content of carbon additives is demanding no more than 2.0 wt.%, often 0.5 wt.% in fact. Nano-Pb/AC composite can overcome this limits by significant inhibition of HER and increase the addition of carbon to a higher level. This offers a possibility to further improve the capacity and power of lead-acid battery.

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